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Stereochemistry of Planarchiral Compounds, Part X[1]:

X-ray Crystal Structures and Absolute Chiralities of Bridged [10]- and [14]Anulenes

Josef Scharf[a], **Karl Schlögl**[a,*], **Michael Widhalm**[a],
Johann Lex[b], **Werner Tückmantel**[b], **Emanuel Vogel**[b,*],
and **Franz Pertlik**[c]

[a] Institut für Organische Chemie, Universität Wien, A-1090 Wien, Österreich
[b] Institut für Organische Chemie, Universität Köln, D-5000 Köln, Bundesrepublik Deutschland
[c] Institut für Mineralogie und Kristallographie, Universität Wien, A-1010 Wien, Österreich

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2,7-Dibromo-1,6-methano[10]anulene (**3**) and 2,9-Dibromo-*syn*-1,6:8,13-diimino[14]anulene (**9**) were quantitatively separated into their enantiomers by chromatography on triacetylcellulose (*TAC*) in ethanol. X-ray structure analysis (*Bijvoet* technique) established the chiralities (+)(*R*)-**3** and (+)(*S*)-**9** for the dextrorotatory enantiomers.

Comparison of the CD spectra allowed the configurational assignment to further optically active [10] and [14] anulenes which were also accessible by chromatography on *TAC*. Conversion of (+)(*R*)-2-bromo-1,6-methano[10]anulene (**2**) into the corresponding methylester (—)-**4** confirmed its previously proposed chirality (—)(*R*).

2,7-Dibromo-1,6-oxido[10]anulene (**7**) and 2,9-dibromo-*syn*-diimino-[14]anulene (**9**) are in contrast to the 2,9-dibromo-*syn*-dioxido-[14]anulene (**10**) optically stable until 250 °C. Consequently their inversion barriers are higher than ~ 42 kcal (176 kJ) mol^{-1}.

The CD spectra of mono and disubstituted anulenes (with C_1 and C_2 symmetry, resp.) are compared: For the [10]anulenes the *Cotton* effect around 330 nm seems to be specific for their configuration with a positive effect indicating (*S*)-chirality and vice versa. Some regularities concerning the chromatographic resolutions are discussed.

(Keywords: Bijvoet method; Circular dichroism; Chemical and chiroptical correlation; Configurational stability; [10]Anulene, 2-Bromo- and 2,7-dibromo-1,6-methano- and 2,7-dibromo-1,6-oxido- and 1,6-imino-; 2,9-Dibromo-syn-1,6 : 8,13-diimino- and dioxido[14]anulene)

Stereochemie planarchialer Verbindungen, 10. Mitt.[1]*: Röntgenkristallstruktur und absolute Chiralität überbrückter [10]- und [14]Anulene*

2,7-Dibrom-1,6-methano[10]anulen (**3**) und 2,9-Dibrom-syn-1,6:8,13-diimino[14]anulen (**9**) wurden durch Chromatographie an Triacetylcellulose (*TAC*) in Ethanol quantitativ in ihre Enantiomeren getrennt. Röntgenstrukturanalyse (*Bijvoet*-Technik) bewies für die rechtsdrehenden Enantiomeren die Chiralität (+)(*R*)-**3** bzw. (+)(*S*)-**9**.

Ein Vergleich der CD-Spektren ermöglichte die Konfigurationszuordnung weiterer optisch aktiver [10]- und [14]Anulene, die gleichfalls durch Chromatographie an *TAC* erhalten worden waren. Umwandlung von (+)(*R*)-2-Brom-1,6-methano[10]anulen (**2**) in den entsprechenden Methylester (—)-**4** bestätigte dessen schon früher vorgeschlagene Chiralität (—)(*R*).

Dibrom-1,6-oxido[10]anulen (**7**) und Dibrom-diimino[14]anulen (**9**) sind im Gegensatz zum Dioxido[14]anulen (**10**) bis 250 °C optisch stabil. Ihre Inversionsbarrieren liegen somit über ~ 42 kcal (176 kJ) mol^{-1}.

Die CD-Spektren von mono- und disubstituierten Anulenen (mit C_1 bzw. C_2-Symmetrie) werden verglichen: Für die [10]Anulene scheint der *Cotton*effekt um 330 nm konfigurationsspezifisch zu sein, wobei ein positiver Effekt (*S*)-Chiralität anzeigt — und vice versa. Einige Regelmäßigkeiten bezüglich der chromatographischen Enantiomerentrennung werden diskutiert.

Introduction

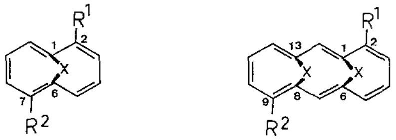
Bridged [10]- and [14]anulenes maintain considerable interest both because of their aromaticity (representing 10- and 14-π systems in accordance with *Hückel*'s rule)[2] and because of their rather unique stereochemistry[3]. The parent compounds (such e. g. **1** and **8**) have C_{2v} symmetry and become (planar)chiral by monosubstitution or by substituting CH in the ring. e.g. by N as in the case of methano[10]azaanulenes[1]. Whereas such compounds have C_1 symmetry, appropriate disubstitution (e.g. in the dibromo derivatives **3**, **9** and **10** or the bisester **5**) leads to structures with C_2 symmetry.

Stereochemical research in this field involves optical resolution, determination of enantiomeric purities, chiroptical properties and of absolute chiralities—together with studies on the configurational stability of enantiomers, especially for the bridged[14]anulenes[4].

First successful results in these respects were gained with 2-substituted 1,6-methano[10]anulenes in 1971[5]. More recently, chromatography on triacetylcellulose in ethanol[1,6]—especially by using a recycling technique[7]—proved to be a powerful tool for the separation of (otherwise unresolvable) enantiomers.

We report here on the enantiomeric separation of some further [10] and [14]anulenes shown in Scheme 1, on the determination of the absolute chiralities of the dibromo derivatives **3** and **9** by the *Bijvoet*-X-ray technique, the chemical and chiroptical configurational correlation of these key compounds with other chiral bridged anulenes (**2**–**7**, **9** and **10**) and on some results on the configurational stabilities of **7**, **9** and **10**.

Scheme 1



	R^1	R^2	X
1	H	H	CH_2
(–)-**2**	Br	H	CH_2
(–)-**3**	Br	Br	CH_2
(+)-**4**	$COOCH_3$	H	CH_2
(+)-**5**	$COOCH_3$	$COOCH_3$	CH_2
(–)-**6**	Br	Br	NH
(–)-**7**	Br	Br	O

	R^1	R^2	X
8	H	H	NH, O
(+)-**9**	Br	Br	NH
(+)-**10**	Br	Br	O

Results and Discussion

Chromatographic Resolutions and Chiroptical Properties

With the exception of **7** all chiral anulenes shown in Scheme 1 could be completely separated into enantiomers on triacetylcellulose in ethanol (see Exp. Part)—at least by the recycling technique[1]. The results are summarized in Table 1 and schematically shown in Fig. 1.

Complete separation establishes also the enantiomeric purities.

The assignment of the chiralities as presented in Table 1, Fig. 1 and Scheme 1 and the apparently stereoselective elution of enantiomers will be discussed below.

Chiroptical properties (specific rotations and circular dichroism, CD) were recorded using the ethanolic solutions from the column after determining concentrations by UV-spectrometry. Because of the strong UV-absorption of the [14]anulenes (Table 2), **9** and **10** had to be measured in high dilution; thus the values are subject to a higher error (appr. 20%) than for all other anulenes (2- max. 5%). Some typical CD-spectra are shown in Figs. 3–5 (for a discussion vide infra).

Configurational Stabilities

Optically active imino and oxido bridged anulenes offer the possibility to investigate their racemization barrier and therefore their configurational stabilities, since inversion of the bridge(s) results in equilibrating the enantiomers.

For the [14]anulene **10** this barrier has recently been determined[4] as $\Delta G = 32$ kcal (134 kJ) mol^{-1}. Similar experiments with optically active **7**

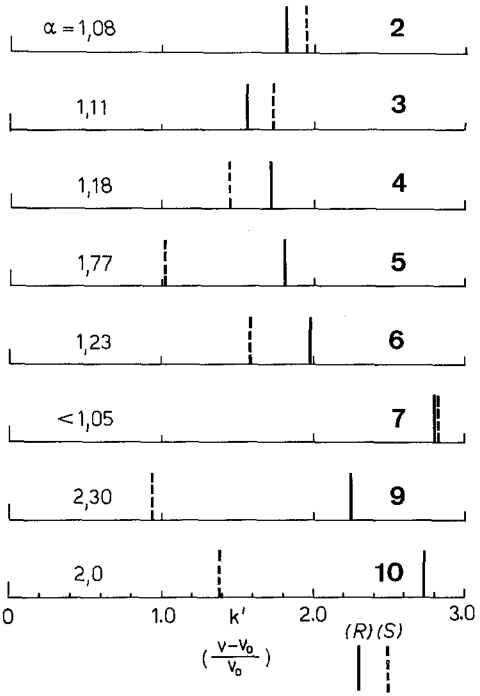


Fig. 1. Chromatographic resolutions of chiral [10]- and [14]anulenes on triacetylcellulose in ethanol

and **9** now established that in these cases the barriers are higher than ~ 42 kcal (176 kJ) mol^{-1} since no racemization could be observed after two hours at 250 °C. Thus obviously the tenmembered ring is more rigid than the fourteen membered one (**7** vs. **10**) and an imino bridge more rigid than the oxidobridge (**9** vs. **10**).

Absolute Chiralities and Configurational Correlations

A first proposal for the absolute configuration of 2-substituted 1,6-methano[10]anulenes[5] was based on results of kinetic resolutions and led to the assignment $(S)_p$ for the dextrorotatory 2-carboxylic acid and all its derivatives [e.g. for the ester (+)-**4**]*.

The dextrorotatory dibromo anulenes **3** and **9**, obtained as the first fractions by chromatography (vide supra), are nicely crystalline and thus

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* For the specification of planar chirality—$(R)_p$ and $(S)_p$—to anulenes see Refs.[3,5].

Table 1. *Optical resolution of bridged [10] and [14]anulenes by chromatography on triacetylcellulose [column 30 × 2.5 cm; TAC 20–30 μm; $p = 1$ bar; 40 °C; 85 ml ethanol (96%)/h]*

Compound No.	V [ml]	k'	α	cycle(s)[7]	$[\alpha]^{20}_{D}$ in ethanol (c) [°]	chirality	established by
2	287 302	1.82 1.96	1.08	8	+50 ± 5 (0.192) —52 ± 5 (0.207)	(*R*) (*S*)	CD-comparison with **3**
3	262 279	1.56 1.73	1.11	8	+17 ± 2 (0.069) —21 ± 2 (0.062)	(*R*) (*S*)	X-ray (Fig. 2)
4	251 278	1.46 1.72	1.18	1	+299 ± 30 (0.02) —335 ± 20 (0.02)	(*S*) (*R*)	(—)-**4** from (+)-**2**
5	207 288	1.02 1.81	1.77	1	+480 ± 50 (0.02) —490 ± 50 (0.02)	(*S*) (*R*)	CD comparison with **4**
6	263 301	1.58 1.95	1.23	2	—273 ± 20 (0.026) +229 ± 20 (0.025)	(*S*) (*R*)	CD-comparison with **3** and **7**
7	390	2.83	<1.05	8	+115 ± 20 (0.013) —102 ± 20 (0.015)	(*R*) (*S*)	CD-comparison with **3**
9	200 333	0.96 2.27	2.3	1	+1 500 ± 300 (0.001)* —1 450 ± 300 (0.001)	(*S*) (*R*)	X-ray (Fig. 2)
10	244 390	1.39 2.73	2.0	1	+1 400 ± 300 (0.001)* —1 600 ± 300 (0.001)	(*S*) (*R*)	CD-comparison with **9**

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* $[\alpha]_{546}$.

Table 2. *Electronic absorption of bridged [10]- and [14]anulenes in ethanol*

Compound No.	λ [nm] (ε)
2	242 (17800), 263 (47800), 312 (6550).
3	233 (14000), 275 (58100), 321 (8770), ca. 380 (1300).
4	210 sh (9000), 264 (35000), 329 (7360), 380 (540).
5	271 (27150), 341 (9410), 400 (1480).
6	229 (14700), 246 (12100), 293 (18500), 330 sh (7640), 410 (630).
7	228 (13200), 276 (59700), 328 (10600), 410 (550).
9	243 (11500), 329 (85100), 370 sh (13600), 400 sh (9830), 570 (700).
10	248 (9800), 320 (141200), 356 (15500), 390 (8920), 402 (9230), 419 (7860), 562 (510), 583 (530).

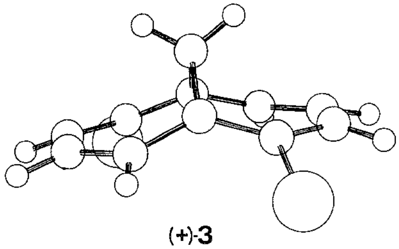
suitable for applying the *Bijvoet* X-ray technique. Their absolute structures (for details see Exp. Part) are shown in Fig. 2: The (+)-enantiomers therefore have the chiralities (+)(*R*)-**3** and (+)(*S*)-**9**, respectively.

These anulenes were used as key compounds for chiroptical and chemical correlations: The very similar CD-spectra of (+)-**3** on the one hand and the dextrorotatory [10]anulenes (+)-**2**, (+)-**6** and (+)-**7** on the other (Fig. 3) permit the conclusion that they all have (*R*)-chirality (cf. Table 1). Comparison of the CD-spectra of the [14]anulenes (+)-**9** and (+)-**10** establishes that both have (*S*)-chirality (cf. Fig. 4).

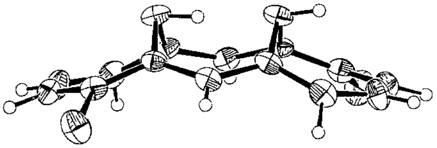
The bromo derivative (+)(*R*)-**2** could be transformed into a laevorotatory ester (—)-**4** by lithiation (at —65 °C), subsequent carboxylation and esterification with diazomethane (for a previous optical resolution of the corresponding carboxylic acid and its CD-spectrum cf. Ref.[5]): this correlation establishes the chirality (—)(*R*)-**4** thus confirming the previous assignment (+)(*S*) for **4** and five other 2-substituted 1,6-methano[10]anulenes[3, 5].

CD-comparison of the mono- and diesters (—)-**4** and (—)-**5** (Fig. 5) include also the latter [(—)(*R*)] into the series of bridged anulenes with known absolute chirality.

Apparently, the change of symmetry from C_1 to C_2 does not change the shape of the spectra (cf. the spectra of **2** and **3** and **4** and **5**, resp.; see Figs. 3 and 5): It leads only to a slight bathochromic shift and an increase in the



(+)-3



(+)-9

Fig. 2. Absolute X-ray structures of (+)-**3** and (+)-**9**

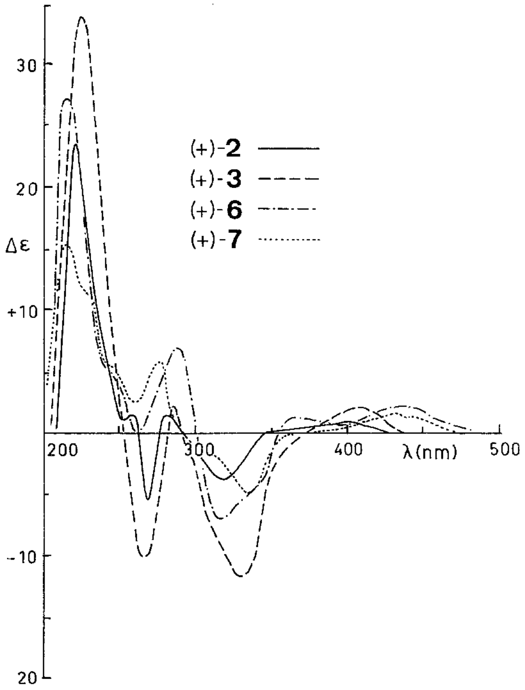


Fig. 3. CD-Spectra of dextrorotatory [10]anulenes **2**, **3**, **6** and **7** in ethanol

$\Delta\,\varepsilon$-values (see also Table 2). As might be expected, the ratio of the overall rotational strengths in going from mono- to disubstitution (cf. **2**:**3** and **4**:**5**) is appr. two (2.2).

A comparison of the CD-spectra of **3**, **6** and **7** on the one hand and of **9** and **10** on the other reveals that the bridges (CH_2, NH or O) have hardly any influence—except on the longwavelength *Cotton* effect above 400 nm (see Figs. 3 and 4).

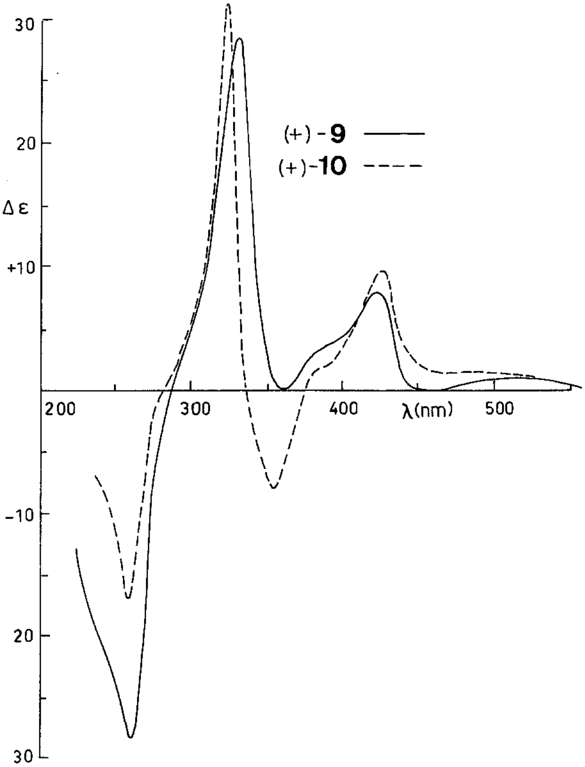


Fig. 4. CD-Spectra of dextrorotatory [14]anulenes **9** and **10** in ethanol

For all [10]anulenes studied so far, the *Cotton* effects between 318 and 340 (corresponding to a ^1L_a electronic transition)^8 seem to be specific for their absolute chirality: A positive effect indicates (*S*)-chirality and vice versa.

The electronic and consequently also the CD-spectra of 2,7-

methano[10]azaanulenes differ considerably from those of the carbocycles. A tentative proposal for the chirality of the former[1]—based on chiroptical comparison with 2-methyl-1,6-methano[10]anulene[5] with its chirality now established—remains still rather speculative.

With regard to the preferred elution of the enantiomers on triacetylcellulose (cf. Table 1 and Fig. 1) some regularities seem remarkable:

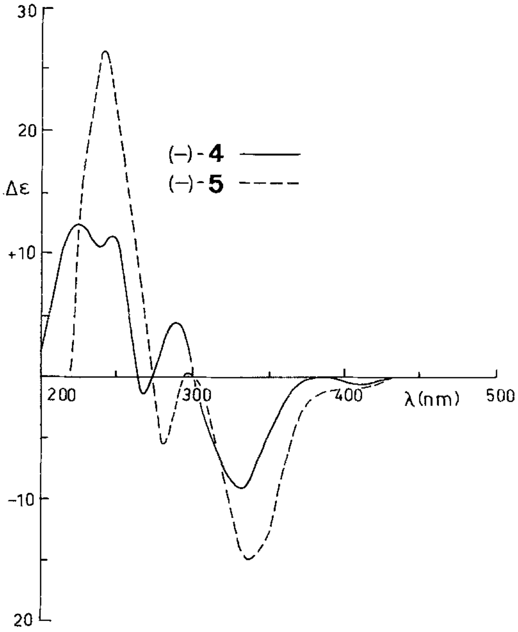


Fig. 5. CD-Spectra of laevorotatory [10]anulenes **4** and **5** in ethanol

If the separation factors α are relatively large (1.18–2.3) such as for **4**, **5**, **6**, **9** and **10**, the (*S*)-enantiomer is eluted first (i.e. less strongly adsorbed), whereas for **2**, **3** and **7** with low enantioselectivity ($\alpha \leqq 1.11$) the sequence is reversed with (*R*)-enantiomers being the first fractions (cf. Fig. 1).

This effect is apparently independent of ring size, the bridge and of symmetry (C_1 or C_2); it may be explained by a simultaneous action of (at least) two different principles of retention. It may be feasible that the less selective mechanism prevails in all cases [with a preferred elution of (*R*)-chirality], but is outweighed in several cases (**4**, **5**, **6**, **9** and **10**) by a more strongly selective mechanism.

Acknowledgements

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Experimental Part

For the preparation of the racemic anulenes see the literature: **2**[9], **3**[9], **4**[5], **6**[10], **7**[11], **9**[12] and **10**[4].

2,7-Di(methoxycarbonyl)-1,6-methano[10]anulene (**5**)

A solution of 50 mg of racem. **3** in 25 ml of dry *THF* was cooled under Ar to —65 °C, then treated with an excess of *n*-butyl-Li in hexane; the mixture was stirred for 30 min and after addition of solid CO_2 for additional 10 min. Then water, ether (20 ml) and dil. hydrochloric acid were added and the dicarboxylic acid extracted with ether. This solution was immediately treated with diazomethane in ether and the ester **5** purified by chromatography on silica gel in ethylacetate-ligroin (15:85). Yield 13 mg (30%) of a yellow oil. $C_{15}H_{14}O_4$ (258.3). MS (*m*/e): 258 (11%), 243 (12), 227 (25), 199 (68), 59 (100). ^{1}H-NMR (250 MHz, $CDCl_3$, δ-values, *TMS*): —0.48 (2 H, s), 3.83 (6 H, s), 7.29 (2 H, t), 8.06 (2 H, d), 8.41 ppm (2 H, d, $J_{H,H} = 9$ Hz).

The preparation of (—)-**4** from (+)-**2** (cf. Table 1 and Fig. 1 for the latter) followed the procedure given for **5**. (—)-**4** was obtained in appr. 25% yield and was identical on TLC and in its MS with the racemic ester. For its CD-spectrum see Fig. 5.

Optical rotations (cf. Table 1) were recorded on a Perkin-Elmer polarimeter 241 in 1 dm cuvettes at 20 ± 0.1 °C in ethanol ($c \approx 0.01$–0.2; for **9** and **10**: 0.001), the CD spectra (see Figs. 3–5) on a dichrograph Mark III (Jobin-Yvon) in 10^{-5}–2.10^{-4} molar ethanolic solutions.

Racemization experiments with (—)-**7** and (+)-**9** were performed as described for (+)-**10** (cf. Ref.[4]).

Crystals of the dextrorotatory enantiomers of **3** and **9** were obtained after chromatography of 20 mg of the racemates on *TAC* (see Table 1 and Fig. 1) by crystallization from ethanol-ether (**3**) and CCl_4 (**9**), resp.

The crystal data, intensity measurements and results of the crystal structure refinements for **3** and **9** together with some further information are summarized in the following. The structures are shown in Fig. 2, atomic parameters given in Tables 3 and 4.

Additional data and information are available upon request.

(+)-**3**: STOE four circle diffractometer. Crystal dimensions: $\varnothing \sim 0.09$ mm, elongation parallel to [100]; range of data: $2° \leqslant 2\Theta \leqslant 60°$. Scan width: 0.96° + ($\alpha_1$, α_2) splitting. MoK_α-radiation. $\mu(MoK_\alpha \sim 78\,cm^{-1})$. Graphite monochromator; measured reflections: 1 620 (—hkL); unique reflections: 1 472; used for refinement: 1 184. $a = 4.4218(5)$, $b = 10.299(1)$, $c = 11.048(1)$ A; $Z = 2$. Space group P2 21 21—D_2^3. Temp. 295 K. $d_{calc} = 1.98\,g\,cm^{-3}$; $R = 0.0331$ [$1\,184\, I \geqslant 3\sigma(I)$]; $R_w = 0.0251$ [$w = 1/\sigma(F)^2$]; No. of variables: 77.

Table 3. *Atomic parameters and temperature factors*[a] *for* (+)-**3**

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br	0.3354 (1)	0.4900 (0)	0.1759 (0)	0.0949 (3)	0.0717 (2)	0.0427 (2)	0.0003 (3)	0.0117 (2)	0.0008 (2)
Cl[b]	0.850 (1)	0.5000 (0)	0.5000 (0)	0.035 (2)	0.064 (3)	0.053 (2)	0.0000	0.0000	—0.004 (2)
C 2	0.167 (1)	0.4431 (3)	0.3283 (3)	0.045 (1)	0.056 (2)	0.036 (1)	—0.007 (2)	—0.008 (2)	0.002 (1)
C 3	0.825 (1)	0.7625 (3)	0.0211 (3)	0.074 (2)	0.040 (2)	0.057 (2)	0.011 (2)	0.002 (2)	—0.002 (1)
C 4	0.069 (1)	0.5426 (3)	0.4048 (3)	0.039 (2)	0.058 (2)	0.040 (2)	0.008 (1)	—0.010 (1)	0.005 (1)
C 5	0.825 (1)	0.8132 (3)	0.1397 (3)	0.057 (2)	0.046 (2)	0.049 (2)	0.003 (2)	—0.004 (2)	0.010 (1)
C 6	0.830 (1)	0.8290 (3)	0.9138 (3)	0.056 (2)	0.046 (2)	0.047 (2)	0.008 (2)	—0.000 (2)	—0.007 (1)
H 1	0.777 (6)	0.674 (3)	0.021 (2)	0.05 (1)					
H 2	0.277 (7)	0.078 (3)	0.973 (3)	0.06 (1)					
H 3	0.768 (6)	0.754 (2)	0.201 (3)	0.04 (1)					
H 4	0.740 (7)	0.789 (3)	0.851 (3)	0.04 (1)					

[a] Anisotropic Factors: $\exp\left[-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} h_i h_j a_i^* a_j^*\right]$.

[b] The *Wyckoff* notation of atom C 1 is 2 a, of all other atoms 4 c.

Table 4. *Atomic parameters and*

	x/a	y/b	z/c	U_{11}
Br	0.9697 (1)	0.7749 (4)	0.1297 (1)	0.0598 (3)
N	0.9105 (3)	0.3038 (10)	0.3821 (4)	0.0485 (16)
C 1	0.9697 (3)	0.5038 (10)	0.3441 (4)	0.0411 (19)
C 2	0.9011 (4)	0.6316 (12)	0.2168 (4)	0.0462 (22)
C 3	0.7892 (4)	0.6771 (11)	0.1536 (4)	0.0405 (20)
C 4	0.7274 (3)	0.6851 (13)	0.2112 (4)	0.0304 (18)
C 5	0.7636 (3)	0.6550 (13)	0.3418 (5)	0.0353 (19)
C 6	0.8637 (3)	0.5118 (10)	0.4347 (4)	0.0392 (18)
C 7	0.9215 (3)	0.5793 (10)	0.5680 (4)	0.0366 (18)

	x	y	z
H 3	0.741 (3)	0.737 (10)	0.065 (4)
H 4	0.661 (3)	0.716 (10)	0.150 (4)
H 5	0.730 (4)	0.831 (19)	0.373 (5)
H 7	0.895 (6)	0.692 (29)	0.591 (7)
HNa[b]	0.844	0.275	0.307
HNb[b]	0.980	0.306	0.458

(+)-**9**: CAD 4 Diffractometer (Enraf-Nonius); MoK$_\alpha$-radiation. No absorption correction. Spacegroup: C 2, $Z = 2$. 1 452 reflections [$I \geqslant 2\sigma(I)$]; (h: 0 to 20, k: 0 to 5, l: —17 to +17 and all *Friedel*-reflections). $a = 14.523(2)$, $b = 4.176(1)$, $c = 12.203(1)$ A, $\beta = 122.66(1)°$. $R = 0.046$ (for the $+x$, $+y$, $+z$ enantiomer), $R = 0.066$ (for $—x$, $—y$, $—z$).

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temperature factors[a] *for* (+)-**9**

U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
0.0719 (3)	0.0504 (2)	0.0027 (3)	0.0395 (2)	−0.0145 (3)
0.0254 (17)	0.0498 (16)	−0.0083 (18)	0.0352 (14)	−0.0079 (16)
0.0255 (16)	0.0384 (18)	0.0034 (15)	0.0273 (16)	−0.0003 (14)
0.0352 (22)	0.0428 (21)	−0.0027 (18)	0.0312 (19)	−0.0039 (17)
0.0403 (23)	0.0363 (19)	−0.0056 (16)	0.0171 (16)	−0.0033 (15)
0.0577 (33)	0.0426 (20)	−0.0116 (17)	0.0160 (17)	−0.0081 (18)
0.0468 (23)	0.0489 (21)	−0.0090 (17)	0.0272 (17)	−0.0073 (18)
0.0311 (17)	0.0446 (20)	−0.0118 (15)	0.0312 (18)	−0.0082 (16)
0.0342 (20)	0.0417 (20)	−0.0063 (14)	0.0273 (17)	−0.0034 (15)

[a] See Table 3.

[b] The difference *Fourier* synthesis does not allow an exact determination of the proton position at nitrogen.

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